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LACTIC ACID RESIN COMPOSITION, PEROXIDE-MODIFIED LACTIC ACID COMPOSITION
AND MOLDING THEREOF

[Nyusankeijushisoseibutsu, kasankabutsuhenseinyusankeijushisoseibutsu, oyobi, sonoseikeibutsu]

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Claims

1. Lactic acid resin composition characterized by comprising 100 parts by weight of lactic acid resin and 0.05-5.0 parts by weight of an organic peroxide having a 1-hour-half-life temperature (Th1) of 70-200°C.
2. Lactic acid resin composition characterized by comprising 100 parts by weight of lactic acid resin and 0.05-5.0 parts by weight of an organic peroxide having a 1-hour-half-life temperature (Th1) of 70-200°C and a hydrogen abstraction coefficient (ϵ) of 10-60.
3. Lactic acid resin composition characterized by comprising 50-97 parts by weight of lactic acid resin, 3-50 parts by weight of an aliphatic and/or aliphatic-aromatic polyester having a glass transition temperature (Tg) below 0°C and 0.05-5.0 parts by weight of an organic peroxide having a 1-hour-half-life temperature (Th1) of 70-200°C and a hydrogen abstraction coefficient (ϵ) of 10-60.
4. Peroxide-modified lactic acid resin composition, characterized in that after reaction of the lactic acid resin composition described in Claim 1 or 2 in a certain manner, $D2/D1$ is 1.0-3.0, where $D1$ is the polydispersity of the lactic acid resin before reaction with peroxide and $D2$ is the polydispersity of the lactic acid resin after reaction with peroxide.
5. Molding characterized by molding from the peroxide-modified lactic acid resin composition described in Claim 4.
6. Molding characterized by being formed after the reaction of the lactic acid resin composition described in Claim 3 in a certain manner.

* [Numbers in right margin indicate pagination of the original text.]

[0001]

Technological field of the invention

The present invention concerns lactic acid resin compositions with excellent moldability, peroxide-modified lactic acid resin compositions and moldings therefrom.

[0002]

Prior art

Recently, with increasing environmental problems, plastic products that decompose with the passage of time and then disappear leaving no adverse effects on the natural environment when discarded in the natural environment have been sought. Usually, conventional plastic products are stable for a long period of time in the natural environment, and with low bulk density, they cause shortening of the life of a waste landfill and damage to the natural landscape and living environment of wild animals and plants.

[0003]

Here, attention is focused on biodegradable plastic materials. Biodegradable plastics undergo hydrolysis and biodegradation in soils and water with gradual disintegration and decomposition, leading ultimately to harmless degradation products via microorganisms. Biodegradable plastics currently used for practical applications include polylactic acid, aliphatic polyesters, modified PVA, cellulose ester compounds, modified starch, and their blends. Each biodegradable plastic material has intrinsic characteristics, and applications are developed according to such characteristics. Of these, lactic acid resins are hard resins and are expected to be used as replacements for hard resins such as polyethylene terephthalate (PET), polystyrene (PS), ABS, etc.

[0004]

However, lactic acid resins have relatively low melt tension, lack strain hardness and have poor processability. With relatively low melt tension and low strain hardness, e.g., in inflation molding of films, bubbles are not stable, while in sheet molding, draw down of sheet occurs during preheating; in blow molding, parison deformation may occur; and in foam molding, bubble breakage occurs extensively.

[0005]

For enhancing melt tension, improvements such as increasing the molecular weight, copolymerization with branched polyfunctional monomers, etc. can be considered. However, increasing the molecular weight may result in excessive melt tension elevation and reduced productivity in extrusion, while branched polyfunctional monomers are not readily available on the industrial scale.

[0006]

In Japanese Kokai Patent Application No. Hei 11[1999]-286570, an attempt was made to raise the melt tension by adding peroxides in foam molding, while lactic acid resins were blended with other aliphatic polyesters in Japanese Kokai Patent Application No. Hei 01[1989]-26658. However, in the above patent applications, the types of peroxides and the reaction product types are not specified, and they were not intended for improving moldability.

[0007]

Problems to be solved by the invention

The objective of the present invention is to provide a lactic acid type resin composition having the original biodegradability of lactic acid type resins as well as excellent processibility and excellent properties, a peroxide modified lactic acid type resin composition, and molding products thereof.

[0008]

Means to solve the problems

Under such circumstances, the highly effective present invention was achieved as a result of intense investigation. This patent application concerns the inventions described in (1)-(5) below.

(1) A lactic acid resin composition comprising 100 parts by weight of lactic acid resin and 0.05-5.0 parts by weight of an organic peroxide having a 1-hour-half-life temperature T_{h1} of 70-200°C.

(2) A lactic acid resin composition comprising 100 parts by weight of lactic acid resin and 0.05-5.0 parts by weight of an organic peroxide having a 1-hour-half-life temperature T_{h1} of 70-200°C and a hydrogen abstraction coefficient ϵ of 10-60.

(3) A peroxide-modified lactic acid resin composition wherein after reaction of the lactic acid resin composition described above in a certain manner, $D2/D1$ is 1.0-3.0, where $D1$ is the polydispersity of the lactic acid resin before reaction with peroxide and $D2$ is the polydispersity of the lactic acid resin after reaction with peroxide. The certain manner described above includes means of heating, radiation irradiation, etc.

(4) Moldings from peroxide-modified lactic acid resins, such as films, sheets, sheet moldings, foam sheets, foam sheet moldings, blow moldings, injection moldings, molded foams, fibers, pipes, plates, plate moldings, etc.

/3

(5) Compositions comprising 50-97 parts by weight of lactic acid resin, 3-50 parts by weight of an aliphatic and/or aliphatic-aromatic polyester with a glass transition temperature T_g below 0°C , and 0.05-5.0 parts by weight of an organic peroxide having a 1-hour-half-life temperature Th_1 of $70-200^{\circ}\text{C}$ and a hydrogen abstraction coefficient ϵ of 10-60.

(6) Moldings formed from the above lactic acid resin compositions in a certain manner such as heating, radiation, etc., such as molded films, sheets, sheet moldings, foam sheets, foam sheet moldings, blow moldings, injection moldings, molded foams, fibers, pipes, plates, plate moldings, etc.

[0009]

Practical embodiments of the invention

Next, the present invention will be explained in detail. Lactic acid resins of the present invention include poly(L-lactic acid) with L-lactic acid as the structural unit, poly(D-lactic acid) with D-lactic acid as the structural unit, poly(DL-lactic acid) with D-lactic acid and L-lactic acid as structural units, and blends thereof. Also, they may be copolymers with an α -hydroxycarboxylic acid and a diol/dicarboxylic acid.

[0010]

For polymerization of lactic acid resins, any known methods including polycondensation polymerization, ring-opening polymerization, etc. may be used. For example, in the polycondensation method, L-lactic acid or D-lactic acid or their mixture is subjected to direct dehydrative polycondensation to obtain lactic acid resins with desired compositions.

[0011]

In ring-opening polymerization, polylactic acids are obtained from lactic acid cyclic dimers, namely, lactides in the presence of a selected catalyst and if needed a polymerization control agent. Lactides include L-lactide that is an L-lactic acid dimer, D-lactide that is a D-lactic acid dimer, and DL-lactide from L-lactic acid and D-lactic acid. If needed, their mixtures are polymerized to obtain lactic acid resins with any desired composition and crystallinity.

[0012]

Furthermore, if needed for improving heat resistance, minor copolymerization components may also be used, including a non-aliphatic dicarboxylic acid such as terephthalic acid and/or a non-aliphatic diol such as bisphenol A-ethylene oxide adduct. For extension of molecular weight, a small amount of a chain extender such as a diisocyanate compound, epoxy compound, acid anhydride, etc. may be used.

[0013]

Other hydroxycarboxylic acid units that can be copolymerized into the lactic acid resins are difunctional hydroxycarboxylic acids such as lactic acid optical isomers (D-lactic acid with L-lactic acid; L-lactic acid with D-lactic acid), glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 2-hydroxy-n-butyric acid, 2-hydroxy-3,3-dimethylbutyric acid, 2-hydroxy-3-methylbutyric acid, 2-methylactic acid, 2-hydroxycaproic acid, etc.; lactones such as butyrolactone, valerolactone, etc.

[0014]

Aliphatic diols that can be copolymerized into the lactic acid resins are ethylene glycol, 1,4-butanediol, 1,4-cyclohexanedimethanol, etc. Aliphatic dicarboxylic acids may be succinic acid, adipic acid, suberic acid, sebacic acid, dodecanedioic acid, etc.

[0015]

The preferred weight-average molecular weight range of the lactic acid resins is 50000-400000, preferably 100000-250000. Lactic acid resins having a weight-average molecular weight below 50000 do not show practically useful properties, while above 250000, melt tension is excessively high, leading to poor moldability.

[0016]

The lactic acid resin compositions in the first embodiment of the present invention are resin compositions obtained by adding 0.05-5.0 parts by weight of an organic peroxide having a 1-hour-half-life temperature (Th1) of 70-200°C to 100 parts by weight of lactic acid resin.

[0017]

The lactic acid resin compositions in the second embodiment of the present invention are resin compositions obtained by adding 0.05-5.0 parts by weight of an organic peroxide having a 1-hour-half-life temperature (Th1) of 70-200°C and a hydrogen abstraction coefficient (ϵ) of 10-60 to 100 parts by weight of lactic acid resin.

[0018]

Organic peroxides are derivatives of hydrogen peroxide (H-O-O-H) with one or both of the hydrogen atoms of the hydrogen peroxide being substituted by an organic radical, and the compounds are characterized by having one or more peroxide bonds (O-O) in the molecule.

[0019]

The peroxides may be ketone peroxides, diacyl peroxides, hydroperoxides, dialkyl peroxides, peroxyketals, alkyl peresters, percarbonates, etc., which are well known.

[0020]

However, for improving moldability of the lactic acid resins, it is necessary to choose compounds having certain properties out of those compounds. Namely, it is essential to select organic peroxide compounds having a 1-hour-half-life temperature (Th1) of 70-200°C, preferably 100-160°C. It is further preferred to select organic peroxides having hydrogen abstraction coefficient (ϵ) of 10-70, preferably 10-60, more preferably 20-60.

[0021]

Here, the 1-hour-half-life temperature (Th1) is the temperature at which the organic peroxide loses one half of its initial weight in 1 h by thermal decomposition. If the 1-hour-half-life temperature (Th1) is below 70°C, the peroxide may decompose even at room temperature and thus is not favored in terms of safety and product life. Furthermore, in the reaction with lactic acid resins, the exothermic reaction occurs too rapidly, leading to decomposition of the resins with localized reaction causing gelation of the resins, and the peroxide may deactivate before reaction with the resins and thus such a peroxide is not

avored. If the temperature is above 200°C, the modification reaction may not proceed under normal reaction conditions. Organic peroxides having a 1-hour-half-life temperature (Th1) of 70-200°C can be chosen from commercially available products satisfying such a condition. For example, PERKADOX BC (Th1 = 132°C) of Kayaku Akzo Co. is available commercially.

/4

[0022]

Moldability can be improved by kneading lactic acid resins with organic peroxides having a 1-hour-half-life temperature (Th1) of 70-200°C. It seems that by kneading certain organic peroxides with lactic acid resins, a crosslinking reaction occurs, resulting in elevation of the viscosity in the linear region.

[0023]

In the present invention, the hydrogen abstraction coefficient (ϵ) is the relative numerical value of the amount of n-pentadecane dimer formed when an organic peroxide at a concentration of 0.2 mol/L in n-pentadecane is decomposed for 30 min at the 15-minute-half-life temperature. Here, the amount formed from 2,2'-azobis(isobutyronitrile) is set at 1. If the hydrogen abstraction coefficient (ϵ) is below 10, the lactic acid resin shows no improvement in moldability, while organic peroxides with a hydrogen abstraction coefficient above 70 are difficult to synthesize and are not readily available at an acceptable cost.

[0024]

Typical examples of an organic peroxides having a 1-hour-half-life temperature (Th1) of 70-200°C and a hydrogen abstraction coefficient (ϵ) of 10-70 are given below: 1,1-di-t-butylperoxycyclohexane

(Th1 = 113°C, ϵ = 24°C) [sic; 24], t-butylperoxy-3,5,5-trimethylhexanoate (Th1 = 114°C, ϵ = 33), 2,2-di-t-butylperoxybutane (Th1 = 116°C, ϵ = 24), t-butylperoxyisopropyl carbonate (Th1 = 117°C, ϵ = 40), t-butylperoxy-2-ethylhexyl carbonate (Th1 = 117°C, ϵ = 40), t-amyl peroxybenzoate (Th1 = 118°C, ϵ = 39), t-butyl peroxyacetate (Th1 = 119°C, ϵ = 43), 4,4-di-t-butylperoxyvaleric acid n-butyl ester (Th1 = 121°C, ϵ = 24), t-butyl peroxybenzoate (Th1 = 122°C, ϵ = 49), 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (Th1 = 134°C, ϵ = 41), 1,3-bis(t-butylperoxyisopropyl)benzene (Th1 = 134°C, ϵ = 55), t-butyl cumyl peroxide (Th1 = 136°C, ϵ = 41), di-t-butyl peroxide (Th1 = 141°C, ϵ = 49), 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3 (Th1 = 141°C, ϵ = 30). Organic peroxides having a 1-hour-half-life temperature (Th1) of 70-200°C and a hydrogen abstraction coefficient (ϵ) of 10-70 can be selected from commercially available products satisfying such conditions. For example, Trigonox 22, Trigonox 42, Trigonox D, etc. of Kayaku Akzo Co. are available commercially.

[0025]

The amount of an organic peroxides added to 100 parts by weight of lactic acid resin is 0.05-5.0 parts by weight, preferably 0.1-3.0 parts by weight. With organic peroxides less than 0.05 part by weight, lactic acid resins show no improvement in moldability, while above 5.0, the resin is totally crosslinked, lacking plasticity with poor processability.

[0026]

In general, the lactic acid resin compositions are reacted by melt kneading at 130-240°C in an extruder or batch kneader. It is also possible for the compositions to be melt-kneaded at a low temperature of 80-130°C or solution-kneaded and then reheated in a mold in a hot air furnace or

irradiated with radiation to carry out a reaction. It is also possible for an intermediate molding to be formed followed by reaction of the peroxide and lactic acid resin. The intermediate molding may be a vacuum molded product from sheets and extrusion sheets for obtaining press molded products.

[0027]

Next, in the present invention, the above compositions are reacted by means of heat, radiation, etc., and it is important to control $D2/D1$ to 1.0-3.0, preferably 1.3-2.2, where $D1$ is the polydispersity of the lactic acid resin before reaction with peroxide and $D2$ is the polydispersity of the lactic acid resin after reaction with peroxide.

[0028]

With a $D2/D1$ ratio below the range described above, the lactic acid resin moldability is not improved, while above the range, the appearance is poor with formation of small and large gels, leading to reduced mechanical properties. Furthermore, even with enhanced melt tension, the strain hardening property is reduced with bleeding of oligomers.

[0029]

For controlling the $D2/D1$ ratio within the range, it is most important that 0.05-5.0 parts by weight of an organic peroxides having a 1-hour-half-life temperature (T_{h1}) of 70-200°C and a hydrogen abstraction coefficient (ϵ) of 10-60 be used. In addition, the effects of heating time, shear rate, water content, the presence of certain metals, and the properties of the reaction residue of peroxides, are strong, and control has to be made taking $D2$ into account.

[0030]

For example, a long heating time in an extruder, the presence of water and an acidic residue of peroxides tend to increase the D2/D1 ratio, while this ratio tends to be smaller with high shear, a short heating time and radiation treatment.

[0031]

The lactic acid resin compositions modified by peroxides (peroxide-modified lactic acid resin compositions) display elevated melt tension, a strain hardening property and good moldability. Thus, the peroxide-modified lactic acid resin compositions are suitable for films, sheets, sheet moldings, foam sheets, foam sheet moldings, blow moldings, injection moldings, foam moldings, fibers, pipes, plates, plate moldings, etc. requiring melt tension during the molding process. /5

[0032]

For example, the following effects can be expected.

- 1) In inflation films, bubbling is stable.
- 2) In sheets, neck down is prevented in extrusion castings.
- 3) In sheet moldings, draw down is prevented in preheating, and the molding thickness distribution is enhanced.
- 4) In foam sheets, the cell structure is uniform and compact with no breakage.
- 5) In foam sheet moldings, draw down is prevented during preheating, and the molding thickness distribution is enhanced.
- 6) In blow moldings, parison draw down is prevented, and the molding thickness distribution is enhanced.

- 7) In injection moldings, flash is prevented.
- 8) In foam moldings, the cell structure is uniform and compact with no breakage.
- 9) In fibers, the drawability is improved during spinning with no fiber breakage.
- 10) In pipes, the shape stability is improved during extrusion.
- 11) In plates, draw down is prevented during horizontal extrusion.
- 12) In plate moldings, draw down is prevented during preheating, and the molding thickness distribution is improved.

[0033]

In the present invention, the lactic acid resin compositions may be blended with aliphatic or aliphatic-aromatic polyester resins with a glass transition temperature T_g below 0°C .

[0034]

The aliphatic polyester resins may be aliphatic polyesters obtained by condensation of aliphatic diols and aliphatic dicarboxylic acids, aliphatic polyesters obtained by ring-opening polymerization of cyclic lactones, synthetic aliphatic polyesters, etc.

[0035]

The above aliphatic polyesters from aliphatic diols and aliphatic dicarboxylic acids can be obtained by condensation polymerization of one or more aliphatic diols such as ethylene glycol, 1,4-butanediol, 1,4-cyclohexanedimethanol, etc. with one or more aliphatic dicarboxylic acids such as succinic acid, adipic acid, suberic acid, sebacic acid, dodecanedioic acid, etc. If needed, desired polymers can be

obtained by jump up with isocyanate compounds, etc. Commercially available raw material pellets can be illustrated by Bionol, a product of Showa Highpolymer Co.

[0036]

For improved heat resistance and mechanical strength, less than 50 mol% (in dicarboxylic acid component) of an aromatic monomer such as terephthalic acid can be copolymerized. Such copolymerized resins are considered to be the aliphatic-aromatic polyesters described in the present invention. Commercially available raw material pellets can be illustrated by Easterbio of the Eastman Chemical Co. and Ecoflex of BASF.

[0037]

For the aliphatic polyesters obtained by the ring-opening polymerization of cyclic lactones, typically one or more of ϵ -caprolactone, δ -valerolactone, β -methyl- δ -valerolactone, etc. are used.

[0038]

The synthetic aliphatic polyesters are obtained from cyclic acid anhydrides and oxiranes, e.g., copolymers of succinic anhydride with ethylene oxide, propylene oxide, etc.

[0039]

When blending aliphatic polyester resins with lactic acid resin compositions, lactic acid resin compositions composed of acid resins, aliphatic and/or aliphatic-aromatic polyesters with a glass transition temperature (T_g) below 0°C and organic peroxides are obtained. In this way, improvement is achieved not only in processability of lactic acid resins, but also in impact resistance and cold resistance.

Also, by adding organic peroxides, compared with simple blends of lactic acid resins and aliphatic and/or aliphatic-aromatic polyesters, mechanical strength and transparency are improved.

[0040]

Compounding ratios (in parts by weight) of the components are preferably lactic acid resin:(aliphatic and/or aliphatic-aromatic polyester):organic peroxide = 50-97:3-50:0.05-5.0 (parts by weight). With a lactic acid resin content above the range given, desired improvements in impact resistance and cold resistance are not realized, while below the range given, the rigidity and scratch resistance are poor.

[0041]

Within the range of retaining effects of the present invention, other additives such as thermal stabilizers, antioxidants, UV absorbers, light stabilizers, pigments, colorants, lubricants, nucleating agents, hydrolysis preventers, inorganic fillers, etc. may be added.

[0042]

For obtaining the compositions, pre-compounding may be done using a biaxial extruder, kneader, Henschel mixer, etc., or the components can be dry-blended and added directly into a molding machine. There are no particular restrictions on molding machines to be used as long as the present invention can be realized.

[0043]

Examples

Next, examples will be illustrated. However, the present invention is not limited to such examples. In the examples, measurements are made under the conditions shown below.

[0044]

1) 1-hour-half-life temperature of an organic peroxides (T_h)

A 0.2 mol/L solution of an organic peroxide is prepared in a benzene solvent. Sample solution is added at 15 mL each into 4 pressure-resistant test tubes. Four pressure-resistant containers are pre-purged with nitrogen, and a sample solution-containing test tube is placed in each pressure-resistant container, which is then capped. The pressure-resistant containers are placed together in a glycerin bath set at a measurement temperature adopted from DSC measurement results and are allowed to stand for 15 min. One pressure-resistant container is removed from the glycerin bath and is immediately immersed in ice water for cooling. After cooling, the test tube is removed from the pressure-resistant container and measured for active oxygen content (AO%) by iodometry. This is the 0 hour value. Then, active oxygen contents (AO%) were also measured similarly after certain periods (2 h, 4 h, 6 h) to obtain the half-life at each temperature. A plot is made with temperature on the horizontal axis and half-life on the vertical axis, and from this graph, the 1-hour-half-life temperature T_h is obtained. For obtaining the hydrogen abstraction coefficient shown below, the 15-min-half-life temperature is also read from the same graph.

/6

[0045]

2) Hydrogen abstraction coefficient (ϵ) of an organic peroxide

The sample solution used is a 0.2 mol/L solution of an organic peroxide in n-pentadecane. This sample solution (20 mL) in a test tube is heated in a glycerin bath at the 15-min-half-life temperature for 30 min, and the amount of n-pentadecane dimer formed is measured and a relative numerical value is obtained based on 1 for the amount of n-pentadecane dimer formed when 2,2'-azobis(isobutyronitrile) is used.

[0046]

3) D2/D1

A Chromatocolumn Shim-Pack Series GPC-800CP of the Shimazu Seisakusho Co. is fitted in a Gel Permeation Chromatography HLC-8120GPC of the Toso Co. Measurement is made with chloroform solvent, a solution concentration of 0.2 wt/vol%, a solution injection of 200 μ L, a solvent flow of 1.0 mL/min, and a solvent temperature of 40°C. The polystyrene-corresponding number-average molecular weight and weight-average molecular weight of lactic acid resin before and after reaction are calculated. The standard polystyrenes used have weight-average molecular weights of 2000000, 670000, 110000, 35000, 10000, 4000 and 600. The polydispersity is obtained by dividing the weight-average molecular weight by the number-average molecular weight. D2/D1 is calculated from D1 for the dispersity before reaction with organic peroxide and D2 for the dispersity after reaction with organic peroxide.

[0047]

4) Strain hardening

Using an SK KRC Kneader N90-1, a product of the Kurimoto Seisakusho Co., a lactic acid resin composition is kneaded at 190°C and 200 rpm, pressed using a 100-t press at 190°C for 10 min and allowed to cool gradually. The press plate obtained is cut to a width x length x thickness of 7 x 55 x 1.5 mm to obtain a sample for a uniaxial extension viscosity measurement. Using an RME of the Rheometrix Co., this sample is measured for uniaxial extension viscosity in a nitrogen atmosphere at 190°C under a constant strain rate (0.5 sec^{-1}). From the resulting graph, strain hardening is calculated using the formula: strain hardening = $(\eta_5 - \eta_1)/\eta_1$, where η_1 = the extension viscosity at a measurement time of 1 sec and η_5 = the extension viscosity at a measurement time of 5 sec.

[0048]

5) Extrusion sheet neck-in

Using a kneading zone-fitted 30 mm ϕ single screw extruder ($1/d = 22$) of the Mitsubishi Heavy Industry Co., a lactic acid resin composition is extruded into a 100 μm -thick sheet at a set temperature of 190°C, a rotation of 30 rpm, an extrusion rate of 3 kg/h, a width of 200 mm and a die lip gap of 1 mm. When the takeup speed is controlled to obtain a sheet with a thickness of 100 μm (takeup speed = about 4 m [sic]), the sheet width immediately after the die outlet is L_1 and the sheet width 20 cm from the die is L_2 . The neck-in is calculated using the formula given below. A neck-in below 10% is preferred in general sheet molding: neck-in (%) = $(L_1 - L_2)/L_2 \times 100$.

[0049]

6) Cell diameter of foam sheet

Using a kneading zone-fitted 30 mm ϕ single screw extruder ($1/d = 22$) of the Mitsubishi Heavy Industry Co., a lactic acid resin composition mixed with 1 part by weight of foaming agent ACDA (azodicarbonamide) is extruded into a 500 μm -thick sheet at a set temperature of 190°C, a rotation of 30 rpm, an extrusion rate of 3 kg/h, a width of 200 mm and a die lip gap of 1 mm. The sheet is cut in the flow direction using a cutter and observed under an optical microscope. The diameters of 10 foam cells within a view are measured visually, and the average value is calculated. The overall state of the foam cells is also observed. In most extruded foam sheets, it is preferred that the cell diameter be below 100 μm and uniform and that no breakage be present.

[0050]

7) Charpy impact strength

A pipe is cut lengthwise to give a sample of width 10 mm x length 80 mm x thickness 4 mm. Using a Charpy impact tester of the Yasuda Seiki Seisakusho Co., the sample is subjected to a notched (notch type A) edgewise test according to JIS K7111. The unit is kJ/m^2 .

[0051]

Application Example 1

Homo-polylactic acid Lacti 5000 (weight-average molecular weight 200000, polydispersity 2.0), a product of the Shimazu Seisakusho Co. was used for the lactic acid resin. A mixture of 100 parts by weight of this lactic acid resin and 0.4 part of lauroyl peroxide (product of the Nippon Kayaku Co., trade name: Laurox, $T_{\text{hl}} = 79^\circ\text{C}$, $\epsilon = 8$) used for an organic peroxide was kneaded at 190°C and 200 rpm

using SK KRC Kneader N90-1, a product of the Kurimoto Seisakusho Co. and extruded into a strand that was then cooled rapidly in water and cut to obtain pellets. The pellets were measured for strain hardening, neck-in and foam cell diameter and a strain hardening of 4.8, neck-in of 12% and foam cell diameter of 120 μm (uniform) were obtained.

[0052]

Application Examples 2-4, Comparative Examples 1-3

Homo-polylactic acid Lacti 5000 (weight-average molecular weight 200000, polydispersity 2.0), a product of the Shimazu Seisakusho Co. was used for the lactic acid resin. This lactic acid resin was mixed with the organic peroxides given in Table 1, kneaded at 190°C and 200 rpm using SK KRC Kneader N90-1, a product of the Kurimoto Seisakusho Co. and extruded into a strand that was then cooled rapidly in water and cut to obtain pellets. The pellets were evaluated similarly as above. The evaluation results are given in Table 1.

/7

Table 1

	(1) 比較例 1	(2) 実施例 2	(2) 実施例 3	(2) 実施例 4	(1) 比較例 2	(1) 比較例 3
(3) 有機過酸化剤	(4) なし	(5) t-ブチルパー オキシベンゾエ ート	(5) t-ブチルパー オキシベンゾエ ート	(6) 2,5-ジメチル2,5-ジ- (t-ブチルパー オキシ)ヘキシン	(7) t-ブチルパーオ キシネオデカノ エート	(8) 2,3-ジメチル 2,3-ジフェニル ブタン
Th 1 (°C)	—	122	122	141	64	259
ϵ	—	49	49	30	4	0
(9) 添加量 (質量部)	—	0.2	0.4	1.5	0.4	0.4
D2/D1	1.02	1.25	1.51	2.02	0.98	1.01
(10) 歪み硬化度	2.6	6.9	11.8	15.8	2.4	2.6
(11) ネックイン率 (%)	18	8	5	3	20	18
(12) 発泡セル径 (μm)	180 (13) 微泡多し	95 (14) 均一	70 (14) 均一	52 (14) 均一	190 (13) 微泡多し	180 (13) 微泡多し
(15) 総合評価	×	○	○	○	×	×

- Key: 1 Comparative Example ____
- 2 Application Example ____
- 3 Organic peroxide
- 4 None
- 5 t-Butyl peroxybenzoate
- 6 2,5-Dimethyl-2,5-di(t-butylperoxy)hexyne
- 7 t-Butyl peroxyneodecanoate
- 8 2,3-Dimethyl-2,3-diphenylbutane
- 9 Amount added (parts by weight)
- 10 Strain hardening
- 11 Neck-in (%)
- 12 Foam cell diameter (μm)

- 13 Extensive breakage
- 14 Uniform
- 15 Overall evaluation

[0054]

Comparative Example 4

Application Example 1 was repeated for pelletization except that 5.5 parts of t-butyl peroxybenzoate ($T_{h1} = 122^{\circ}\text{C}$, $\varepsilon = 49$) was used for the organic peroxide. Due to excessive modification of the resin by the organic peroxide, the extruded melt became a gel, making stable obtention of a strand difficult. Pelletization failed. The strand had a $D2/D1$ of 3.6.

[0055]

Comparative Example 5

Lacti 5000 of the Shimazu Seisakusho Co. was dry blended at 8/2 with Easterbio with a T_g of -30°C from the Eastman Chemical Co. and extruded through a 45 mm ϕ single screw extruder of the Claus Maffai Co. fitted with a 25 mm ϕ die and a DISK Type Former of the Batten Co. at an extrusion resin temperature of 190°C and a screw rotation of 70 rpm to obtain a pipe with an outer diameter of 25 mm ϕ and a thickness 4 mm. The pipe was taken up without water cooling at the die outlet while using a cylindrical support. With insufficient melt tension, the pipe sagged from its own weight. The charpy impact strength was 3.5 kJ/m^2 .

[0056]

Application Example 5

Comparative Example 4 was repeated to obtain an extruded pipe except that 0.5 part by weight of 2,2-di-*t*-butylperoxybutane ($T_{h1} = 116^{\circ}\text{C}$, $\varepsilon = 24$) was used as the organic peroxide. With a high melt tension, a pipe was obtained without deformation with good roundness. The charpy impact strength was 4.2 kJ/m^2 , a significant increase over the case without the addition of an organic peroxide.

[0057]

Effect of the invention

As described in detail, according to the present invention, lactic acid resin compositions, peroxide-modified lactic acid resin compositions and molded products thereof having excellent processability and excellent physical properties in addition to the biodegradability intrinsic to lactic acid resins can be provided.